Effects of Mordenite Support on Photodegradation of Gaseous Organic Compounds over TiO_2 Photocatalyst

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(Received December 8, 1998)

Effects of mordenite as a support material for TiO_2 on photodegradation rates of gaseous propionaldehyde, acetone, and propane were investigated using TiO_2 (50 wt%)-loaded mordenite as a photocatalyst in reference to unsupported TiO_2. The supported photocatalyst allowed adsorption of all the substrates several times greater than the unsupported photocatalyst, resulting in higher photooxidation rates for them. Detailed analysis suggests that the enhancement of the decomposition rate caused by the use of mordenite support is more remarkable for lower amounts of adsorption of the substrates on the support. The concentration of oxygen was found to have little influence on the photodegradation rates, suggesting that the rate of degradation of the organic substrates was not decided by photogenerated electron transfer processes but by the consumption of photogenerated holes by adsorbed organic substrates.

Photocatalysis of semiconductor particles, especially of titanium dioxide, has been attracting much attention because of possible applications to abatements of pollutants in water and air.[1—8] We have demonstrated utilities of adsorbents as supports for TiO_2 as the means of enhancing apparent rates of photomineralization of organic substances of dilute concentrations such as gaseous pyridine[9] and propionaldehyde,[10,11] and propyzamide dissolved in water.[12—14] The adsorbent supports collect substrates from air or water, resulting in high-concentration environments of substrates around loaded TiO_2, and thereby the photodegradation rates are increased. In a series of studies on photodegradation of gaseous propionaldehyde, TiO_2-loaded (50 wt%) mordenite films had the highest photocatalytic activity among several kinds of supported photocatalysts tested.[10,11] The mordenite has such an adsorption strength for propionaldehyde that allows a high adsorption, yet does not greatly retard the diffusion of adsorbed propionaldehyde from adsorption sites to the loaded TiO_2.

So far, our studies on photodegradation of gaseous substrates were fixed to propionaldehyde only and its concentration was also fixed. By this reason little is known about the influence of the kinds of substrates and their concentrations on the enhancement of the photodegradation rates. In this paper, comparative studies on the photodegradation of propionaldehyde, acetone, and propane with use of TiO_2-loaded mordenite photocatalysts are reported to clarify the role of the adsorbent supports in the photodegradation rates.

Experimental

Materials and Preparation of Photocatalyst Films. Commercially available mordenite powder (Tosoh TSZ-640NAA; dry composition 4.9 Na_2O : 4.7 Al_2O_3 : 90 SiO_2) was used as a support material for TiO_2. Mordenite is a kind of zeolite having a one-dimensional channel with pore openings of 7 Å. The size of mordenite powder ranged from 0.5 to 5 μm with average diameter of 2 μm, as measured by SEM observations. Propionaldehyde (Wako Pure Chemicals, Japan) was purified by distillation. The methane (99.7% purity), ethane (99.5% purity), and propane (99.5% purity) used were GC standard gases obtained from GL Sciences (Japan). All other chemicals used were purchased from Wako Pure Chemicals (reagent grade) and used as received. Water was prepared by twice distillation of deionized water.

The TiO_2 content of the supported photocatalyst was fixed to 50 wt% in this study. Titanium dioxide (50 wt%)-loaded mordenite films (TiO_2/mordenite) were prepared by hydrolysis of titanium tetraisopropoxide to give TiO_2 colloid (15 g L^{-1}), to which an equivalent amount of mordenite powder was added, followed by stirring for 1 h. After repeating centrifugation and washing of the precipitates, solids were separated from the suspension, and calcined, as described previously in detail.[10] TiO_2/mordenite films were prepared on a borosilicate glass plate (4 cm long × 1 cm wide), as described also in our previous paper.[10] Unsupported TiO_2 films and mordenite films were prepared using similar procedures. The amount of coated photocatalyst was adjusted to 1.0 mg cm^{-2} for TiO_2/mordenite, and 0.5 mg cm^{-2} for unsupported TiO_2 and for naked mordenite. The thickness of the TiO_2/mordenite and the unsupported TiO_2 film were about 5 and 2.5 μm, respectively, as measured by observations with a scanning electron microscope (Hitachi S-800). It has been reported in our previous paper[10] that BET specific surface areas measured by Ar adsorption of calcined photocatalyst powder were 293 m^2 g^{-1} for TiO_2/mordenite and 178 m^2 g^{-1} for unsupported TiO_2, respectively, while that of mordenite powder was 375 m^2 g^{-1}, which was mainly assigned to the inner surface area due to micropores. XRD patterns showed that the obtained titanium dioxide particles were mostly anatase. The diameters of the prepared TiO_2 particles were measured with a Hitachi H-9000 transmission microscope at an operating voltage of 300 kV.

Adsorption and Photodegradation Experiments. Experimental setups for studies on adsorption and photodegradation of organic vapors were essentially the same as those reported previously.[10] A cylindrical photoreactor (total volume of 15 mL) made of Pyrex glass was equipped with a gas-tight stop cock sealed

with a silicon rubber septum. All the experiments were conducted at room temperature (25 °C). Irradiation was done normal to the photocatalyst film surface using a 10 W blacklight fluorescent lamp (NEC) that emitted light of wavelengths ranging from 300 to 400 nm with its peak at 352 nm. The incident light intensity was 1.8 mW cm^{-2} as measured by a thermopile (Eppley Lab. E-6). The photocatalyst films allowed light transmittance of about 1% of incident light at 352 nm as measured by a photodiode array spectrometer (HP 8452A). No correction was made for light scattering.

Prior to each experiment, humid air containing 4.6 Torr H_2O (1 Torr = 133.322 Pa), which was prepared by passing through a water tank kept at 0 °C, was passed through the photoreactor for 10 min in which the photocatalyst film was installed, and then the photocatalyst film was irradiated for more than 2 h. These procedures were repeated until no measurable amount of carbon dioxide was evolved from the photocatalyst films. Finally, after passing the humidified air again through the cell for 10 min, the cell was closed, and an appropriate amount of organic vapor (propionaldehyde, acetone, and propane) was injected using a gas-tight syringe. The amount of adsorption under equilibrium condition S_{ads} was determined by monitoring changes in the concentration of gaseous substrates in the cell. When photodegradation experiments were carried out, the cell was kept in the dark for typically more than 4 h before irradiation to allow adsorption equilibrium. During the photodegradation experiments the composition of gas phase in the cell was analyzed intermittently by sampling 50—100 μL each.

The amount of carbon dioxide evolved was analyzed by a Yanaco G2800T gas chromatograph equipped with a thermal conductivity detector (TCD) and a Porapak T column (Waters; 100/120 mesh, Sus 3 mm i.d. ×2 m) operated at 100 °C. Helium was used as a carrier gas and its flow rate was 11 mL min^{-1}. Analysis of gaseous substrates was performed using a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector (FID) and a Gaskuropak 54 column (GL Sciences, Japan; Sus 3 mm i.d. ×1.5 m). The column temperature was kept at 120 °C. Helium was used as a carrier gas and its flow rate was 45 mL min^{-1}.

Besides analysis of the gas phase, water soluble organic products adsorbed on the photocatalyst films were measured in separate experiments. Five milliliters of water was poured into the cell, and the photocatalyst was removed from the glass plate with a spatula to give a suspension, followed by centrifugation, and the obtained supernatant was used for analysis. The analysis was done using the same GC-FID as mentioned above which was equipped with a capillary column (J & W Scientific DB-WAX column; 30 m long, 0.32 mm i.d., 0.5 μm film thick). The injection was made in the split mode (split ratio of 1 : 3). The column temperature was programmed as follows: 35 °C for 5 min, 35—155 °C at 10 °C min^{-1} and 155 °C for 10 min. Helium was used as a carrier gas and the flow rate was 36 cm s^{-1}.

Photodegradation experiments were also carried out under different compositions of oxygen and nitrogen. For this purpose, the cell was purged with mixed gases of O_2 and N_2 for more than 1 h, and then the mixed gases containing 4.6 Torr H_2O flowed through the cell for 10 min. After the stopcocks of the cell were closed, organic vapors were injected into the cell using a syringe. The composition of the mixed gas was analyzed by gas chromatography (Yanaco G2800T, Molecular Sieve 5A column (30/60 mesh) with TCD; column temperature: 40 °C, carrier gas: He).

Results and Discussion

Gas Adsorption. Observations by a transmission electron microscope of photocatalyst powders showed that small TiO_2 particles having diameters about 50—80 Å were aggregated regardless of the kind of photocatalysts used in this study. Furthermore in the case of TiO_2/mordenite, it was found that the TiO_2 particles were aggregated on mordenite particle surfaces and no TiO_2 particles were present in micropores of mordenite. These findings are in good agreements with the results obtained by BET surface areas measurements of the photocatalysts, that the specific surface area of TiO_2/mordenite powder was roughly equal to that expected for 1 : 1 mixture of the mordenite powder and the unsupported TiO_2 powder, as already reported in our previous paper.[10] Since the TiO_2 was prepared using the same procedures between TiO_2-loaded mordenite and unsupported TiO_2, it may not be unreasonable to assume that the photocatalytic activities of both kinds of TiO_2 were almost the same.

The amounts of adsorption (S_{ads}) per unit apparent surface area of the photocatalyst films under equilibrium conditions of three kinds of gaseous organic compounds, propionaldehyde, acetone, and propane, were determined as a function of the concentration of these gases (C_{eq}) in the air containing 4.6 Torr H_2O. The results are shown in Fig. 1 for the case of propionaldehyde, as an example. By applying the obtained results to Langmuir adsorption isotherm given by Eq. 1, adsorption constant K_{ads} for the gaseous substrates and the maximum amount of adsorption on the photocatalyst film S_{ads}^{max} were determined.

$$C_{eq}/S_{ads} = 1/(K_{ads}S_{ads}^{max}) + C_{eq}/S_{ads}^{max}. \quad (1)$$

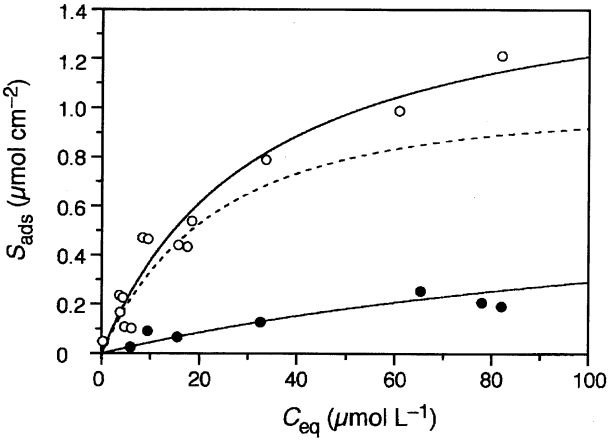

Fig. 1. The amount of adsorbed propionaldehyde obtained under adsorption equilibrium in the dark as a function of the concentration in gas phase for 0.5 mg cm^{-2} unsupported TiO_2 (closed circles) and 1.0 mg cm^{-2} TiO_2 (50 wt%)/mordenite (open circles) films (1 cm×4 cm). A cell of 15 mL capacity contained 21% O_2, 79% N_2, and 4.6 Torr water vapor besides propionaldehyde. Solid curves were obtained by applying adsorption parameters shown in Table 1 to the Langmuir adsorption isotherm. Dotted curve gives the amount of adsorbed propionaldehyde on mordenite of 1.0 mg cm^{-2} TiO_2/mordenite film under adsorption equilibrium.

Table 1 shows results obtained by applying least squares fits. Solid curves given in Fig. 1 are adsorption isotherms obtained using the parameters shown in Table 1 for propionaldehyde. It is recognized that (1) the amount of adsorption was much greater at the TiO_2/mordenite than at the unsupported TiO_2 for all the substrates. This fact probably resulted from the adsorption of substrates in micropores of mordenite, since the size of micropores (7 Å) was larger than the diameters of the cross section of the substrates used. (2) the unsupported TiO_2 gave comparable K_{ads} and S_{ads} between propionaldehyde and acetone, the same being true for the TiO_2/mordenite films, and (3) propane has much less affinity for adsorption, as compared with propionaldehyde and acetone.

From these results, we can estimate the local distributions of adsorbed substrates on the TiO_2/mordenite photocatalyst films under equilibrium. If it is assumed that TiO_2 of the TiO_2/mordenite has the same affinity for adsorption of a gaseous substrate as the unsupported TiO_2 film, the amount of substrate adsorbed on mordenite of the TiO_2/mordenite films (S_{ads}(mor)) is obtained by subtracting the amount of adsorbed substrates on the unsupported TiO_2 ($S_{ads}(TiO_2)$) from that on the TiO_2/mordenite film ($S_{ads}(TiO_2/mor)$).

$$S_{ads}(mor) = S_{ads}(TiO_2/mor) - S_{ads}(TiO_2). \quad (2)$$

The calculated S_{ads}(mor) as a function of C_{eq} is shown for propionaldehyde as a dotted line in Fig. 1, as an example. Most of the substrate are adsorbed on the mordenite part of the film when the adsorption equilibrium is attained. The same was true for acetone and propane adsorption. Calculations showed that among the total amount of adsorption, more than 90% for propionaldehyde, more than 89% for acetone, and more than 93% for propane were adsorbed on the mordenite of the TiO_2/mordenite for the total concentration of substrates smaller than 130 μmol L^{-1}, which was used for photooxidation experiments in this study.

Photodegradation Behaviors. Photodegradation experiments of organic compounds listed in Table 1 were done under a fixed condition of O_2 = 21% and 4.6 Torr humidity. Figure 2(a) shows time courses of decreases in the concentrations of propionaldehyde, acetone, and propane, the initial concentration of which was 130 μmol L^{-1} for all cases, and Fig. 2(b) shows those of evolved CO_2. The concentration of substrates shown in Fig. 2(a) is the sum of those collected both from the gas phase and from the photocatalyst films. The amount in the gas phase was experimentally determined, while the amount on the photocatalyst films was evaluated using the adsorption parameters shown in Table 1.

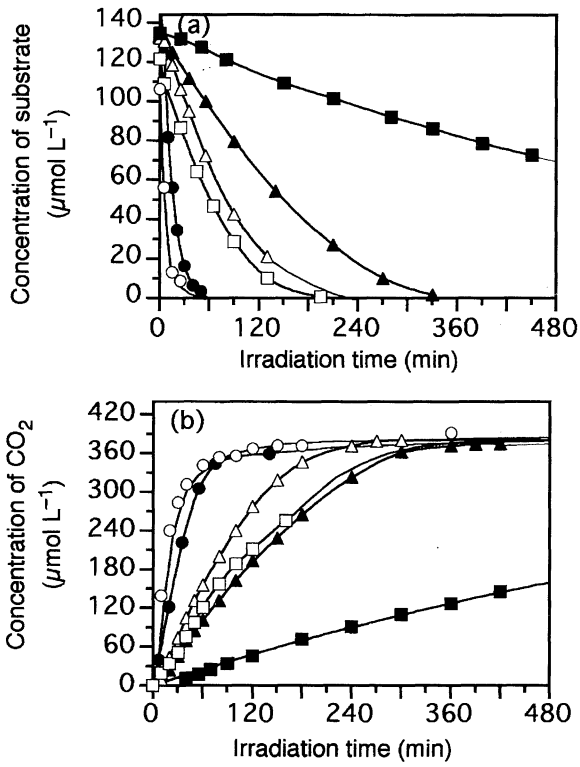

Fig. 2. Time profiles of (a) decrease in the concentration of substrates and of (b) CO_2 evolution. Closed symbols give results obtained at the unsupported TiO_2 and open symbols give those obtained at the mordenite-supported TiO_2 photocatalyst films. Substrates: circles, propionaldehyde; triangles, acetone; squares, propane. The concentration of substrate given in this figure is the sum of that obtained from both gas phase and the photocatalysts. The amount of photocatalyst in the cell was the same as that given in Fig. 1. The substrates were injected in atmospheric air containing 4.6 Torr H_2O. An initial concentration of substrate was 130 μmol L^{-1}.

After sufficiently long time of irradiation, no appreciable amounts of organic compounds were observed in gas phase and stoichiometric amounts of carbon dioxide were obtained instead for all the substrates investigated. Furthermore if the photodecomposition experiments were performed more than 10 times using the same photocatalysts and under the same conditions, essentially the same curves as Fig. 2 were obtained in both kinds of photocatalysts used, indicating that the photocatalytic activities were not deteriorated during the photodecomposition experiments. It was confirmed that no decrease in the amount of the substrates and no evolution of

Table 1. Adsorption Parameters Obtained at 0.5 mg cm^{-2} Unsupported TiO_2 Film and 1.0 mg cm^{-2} TiO_2 (50 wt%)/Mordenite Film

Photocatalyst film	Propionaldehyde		Acetone		Propane	
	K_{ads}	S_{ads}^{max}	K_{ads}	S_{ads}^{max}	K_{ads}	S_{ads}^{max}
	μmol^{-1}L	μmol cm^{-2}	μmol^{-1}L	μmol cm^{-2}	μmol^{-1}L	μmol cm^{-2}
Unsupported TiO_2	0.0064	0.75	0.0047	0.73	0.0018	0.053
TiO_2/mordenite	0.031	1.6	0.026	1.3	0.0073	0.24

CO_2 occurred when irradiation was done in the absence of TiO_2 (using bare glass plates or TiO_2-free mordenite film) after adsorption equilibrium was attained.

As shown in Fig. 2, the rate of decrease of substrate and that of CO_2 evolution were greater at the mordenite-supported photocatalyst films than at unsupported TiO_2 films for all the substrates examined. Such differences are believed to have resulted from differences in the amount of adsorbed substrates between the two kinds of photocatalyst films, as already discussed in our previous papers.[10,11]

The initial photocatalytic reaction rates of the three kinds of gaseous substrates were determined for various concentrations of substrates, using the time courses as shown in Fig. 2. Figure 3 shows the initial rate of substrate decrease (R_{deg}) and the initial rate of CO_2 evolution (R_{CO_2}) given by the unit apparent surface area of the photocatalyst films as a function of initial atmospheric concentration of the substrates obtained after adsorption equilibrium. The amount of adsorbed substrate on TiO_2 particles would be the same between the supported and unsupported photocatalysts if the atmospheric concentration is the same. Comparisons under such conditions reveal that both the rate of decrease of the substrates and that of the evolution of CO_2 were higher at the supported photocatalysts than at the unsupported ones for all the substrates examined. Furthermore, the observed rates were different among the three kinds of substrates. There seem to be at least two factors which are responsible for these. One is differences in the amount of adsorption and the other is differences in the reactivity for photocatalytic destruction.

Intermediate Products. The complete oxidation of the three organic compounds are given by Eqs. 3, 4, and 5.

$$\text{propionaldehyde}: \quad CH_3CH_2CHO + 4O_2 \rightarrow 3CO_2 + 3H_2O, \qquad (3)$$

$$\text{acetone}: \quad CH_3COCH_3 + 4O_2 \rightarrow 3CO_2 + 3H_2O, \qquad (4)$$

$$\text{propane}: \quad CH_3CH_2CH_3 + 5O_2 \rightarrow 3CO_2 + 4H_2O. \qquad (5)$$

As these equations show, a ratio of R_{CO_2} to R_{deg} of 3 is expected at initial stage of irradiation for all cases if no stable intermediates are photo-produced. However, as shown in Fig. 3, experimentally determined R_{CO_2}/R_{deg} was about 1 for the case of propionaldehyde, suggesting that some stable intermediates were formed during the photodegradations. On the other hand, R_{CO_2}/R_{deg} of about 2 and 2.7 were obtained for propane and acetone, respectively.

Figure 4 shows changes in the gaseous concentration of propionaldehyde caused by its photodecomposition over the unsupported TiO_2 photocatalyst. Acetaldehyde was formed as a major intermediate, and its concentration increased with irradiation until a large fraction of propionaldehyde disappeared, and then decreased, while the concentration of CO_2 monotonously increased. Other minor intermediates, such as methanol and ethanol, also had similar behaviors to acetaldehyde. These results were in good conformity with that of $R_{CO_2}/R_{deg} \approx 1$.

Table 2 shows the amount of intermediates contained in

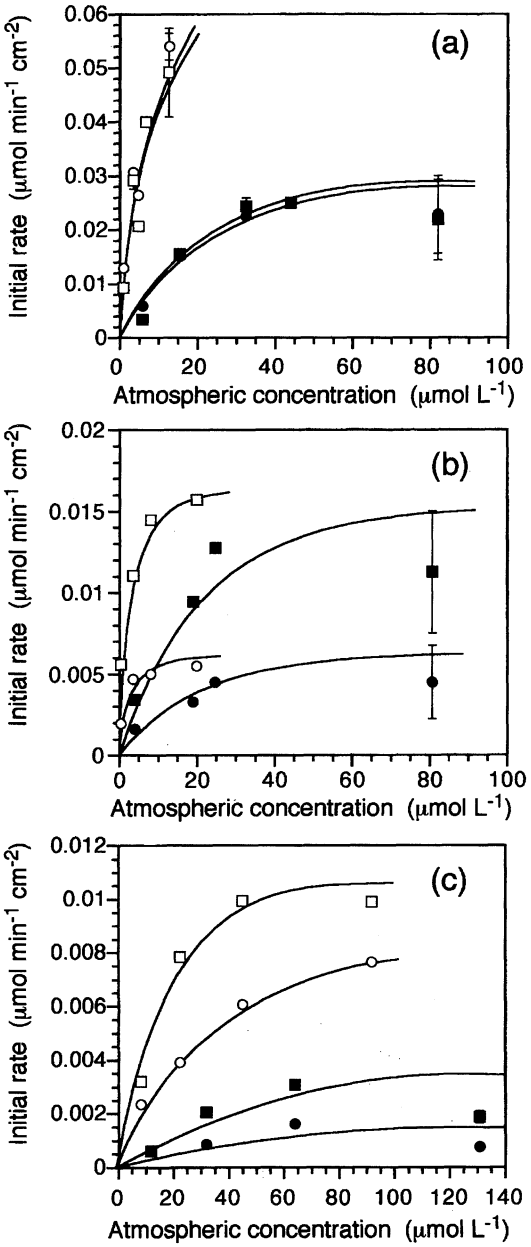

Fig. 3. Initial rates of decrease of the substrates (R_{deg}, circles) and initial evolution rates of CO_2 (R_{CO_2}, squares) obtained at the unsupported TiO_2 (closed symbols) and the TiO_2/mordenite (open symbols) films as a function of atmospheric concentration of substrates. (a) propionaldehyde, (b) acetone, and (c) propane. Experimental conditions were the same as those given in Fig. 2 except that initial concentrations of substrates were varied.

the gas phase and adsorbed on unsupported TiO_2 photocatalyst films. It is seen that the total number of carbons detected were almost equal to that of substrates injected in the reaction cell (5.85 μmol) at the three kinds of substrates, indicating that the substances and their amounts shown in the table give correct information about the photodegradation reaction. It should be noted that the fraction of acetaldehyde detected in the gas phase was much larger than that of propionaldehyde. This fact indicated that the photodegradation rate of acetal-

Table 2. Products Collected from Gas Phase and from the TiO_2 Photocatalysts at the Time When the Total Concentration of Substrate Became One-Half the Initial Value ($t = t_{1/2}$) of 130 μmol L^{-1} [a] with the Photodegradation over Unsupported TiO_2 Photocatalyst Film

Substrate	$t_{1/2}$ min	Products	Gas phase μmol	TiO_2 film μmol	Total carbon atom[b] μmol
Propionaldehyde	15	Propionaldehyde	0.62	0.40	5.90
		Acetaldehyde	0.41	0.21	
		Propionic acid	n.d.[c]	0.008	
		Acetic acid	n.d.	0.10	
		Ethanol	<0.03	n.d.	
		Ethane	<0.03	n.d.	
		Methanol	<0.03	n.d.	
		Methane	<0.03	n.d.	
		CO_2	1.2	n.d.	
Acetone	120	Acetone	0.55	0.60	6.25
		CO_2	2.8	n.d.	
Propane	480	Propane	1.08	n.d.	5.79
		Acetone	0.02	<0.03	
		CO_2	2.4	n.d.	

a) The amount of carbon atoms injected in the cell as substrates were 5.85 μmol for three kinds of substrates used. b) Total amounts of carbon atoms which was detected as products. c) n.d.: not detected.

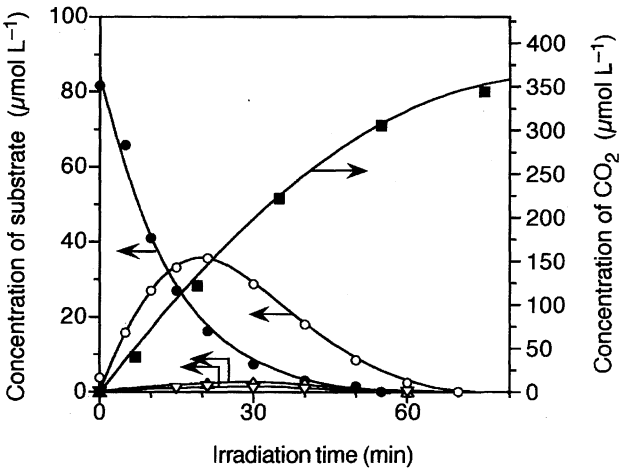

Fig. 4. Time course of the gaseous concentration of propionaldehyde (●), acetaldehyde (○), ethanol (▽), methanol (△), and carbon dioxide (■) by irradiation to unsupported TiO_2 film. The prorionaldehyde was injected in atmospheric air containing 4.6 Torr H_2O. An initial concentration of prorionaldehyde was 130 μmol L^{-1}.

dehyde should be small due to its weak adsorption ability, so that propionaldehyde was predominantly photodecomposed as long as a large amount of propionaldehyde was available in the cell. Photooxidation of acetone did not give any recoverable intermediates, as suggested from $R_{CO_2}/R_{deg} \approx 2.7$, the results being in agreements with published results by Peral et al.,[15] while a trace amount of acetone was detected as an intermediate of propane photodegradation (Table 2) as expected from $R_{CO_2}/R_{deg} \approx 2$, the results being also consistent with already reported results.[16] It is inferred from these results that intermediate products of photooxidation of acetone, if produced, are more rapidly photodegraded to CO_2 than acetone.

Effects of Oxygen. The effects of oxygen concentrations on the initial photodecomposition rates of the three kinds of substrates were investigated. The initial concentration of the substrate used was 130 μmol L^{-1}. It was found that the amounts of adsorbed organic substrate on mordenite-supported and unsupported TiO_2 obtained under adsorption equilibrium were not changed by the oxygen concentrations. As shown in Fig. 5(a), the initial rates of decrease of the three kinds of substrates (R_{deg}) at the TiO_2/mordenite films were also little influenced by the oxygen concentrations. The initial rate of CO_2 evolution (R_{CO_2}), however, was influenced by the oxygen concentrations for smaller than 20 mol%, as shown in Fig. 5(b). Similar results were obtained for the unsupported TiO_2 films, too. The results obtained in this study are in rough accord with published results that the rate of photooxidation of gaseous acetone[17] and 2-propanol[18] became independent of the concentration of oxygen if the concentration exceeds a certain threshold value.

As reactions (3)—(5) indicate, oxygen molecules are involved in the oxidation of organic molecules to produce CO_2. Photocatalyzed oxidation of an aliphatic compound (RH) is thought to be initiated by reaction with a valence band hole (h^+_{VB}) or with a photogenerated hydroxyl radical ($OH^\bullet$) on the irradiated TiO_2 surface to give a carbon-centered radical ($R^\bullet$).

$$RH + h^+_{VB}(\text{or } OH^\bullet) \rightarrow R^\bullet + H^+(\text{or } H_2O). \quad (6)$$

Attack by molecular oxygen to the radical would give peroxy radicals or other intermediates which are further oxidized finally to give CO_2.[19]

$$R^\bullet + O_2 \rightarrow ROO^\bullet \rightarrow\rightarrow CO_2. \quad (7)$$

Moreover, oxygen molecules seem to pick up conduction band electrons to ensure charge separation.

$$e^-_{CB} + O_2 \rightarrow O_2^{\bullet -}. \quad (8)$$

The finding that the oxygen concentration more significantly

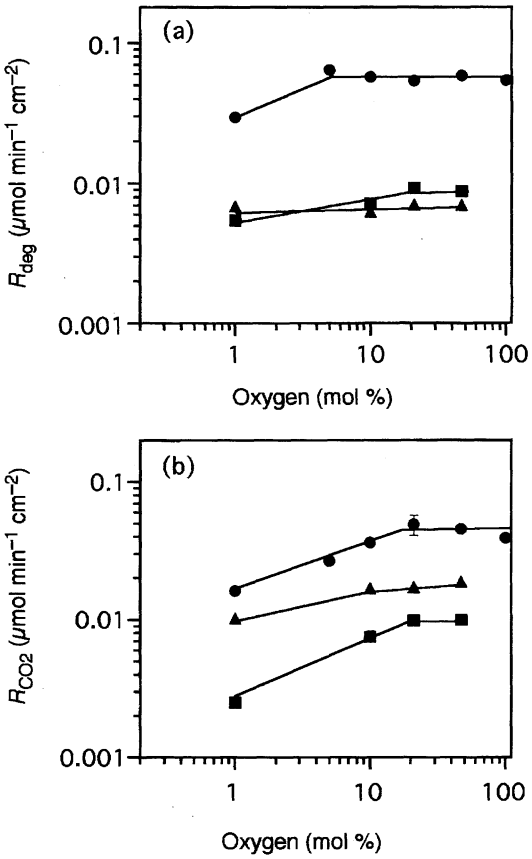

Fig. 5. Dependence of initial rates of decreases in the concentration of organic compounds (a), and of CO_2 evolution (b) on oxygen concentration in the gas phase at the TiO_2/mordenite film as photocatalyst. Circles, propionaldehyde; triangles, acetone; squares, propane. The initial concentration of injected substrate was fixed to 130 μmol L^{-1}.

influences the initial rate of CO_2 evolution rather than on the initial rate of decrease of substrates might reflect a situation in which oxygen molecules are involved directly in carbon dioxide production. When R_{CO_2} becomes saturated with increasing oxygen, photooxidation rates of substrate are considered to be determined by a hole-consuming process as given by reaction (6), as already discussed by Grela et al. under weak irradiation intensity.[20]

Rate Enhancement Effect of Mordenite. As shown in Fig. 3, the mordenite-supported photocatalyst was effective in enhancing the photooxidation rates of the three gaseous organic compounds examined. The substrates adsorbed on mordenite are supplied to irradiated TiO_2 particles by diffusion for being photodecomposed, as reported in our previous papers.[10,11] Accordingly, the observed differences of values of R_{deg} between the supported and unsupported photocatalysts as shown in Fig. 3 are attributed to differences in the amount of the substrates on TiO_2 surfaces. Under the conditions used in this study, the distance for the adsorbed molecules to be diffused seems less than a radius of the largest mordenite particle, 2.5 μm.

However, the rate enhancement brought by the use of mordenite was different among the three kinds of substrates. For example, if comparisons are made at 10 μmol L^{-1} of atmospheric concentration, the initial photodegradation rate (R_{deg}) was enhanced by the case of the mordenite support to about 5 times for propionaldehyde, about 3 times for acetone, and about 6 times for propane. Such difference might arise from differences in the flux of substrates from the support to the loaded TiO_2, because the concentrations of adsorbed substrates are different at the same atmospheric concentration of 10 μmol L^{-1}.

To get more exact information of the effects of the adsorption of substrates on the adsorbent support at a given gaseous concentration, the data of the initial photodegradation rates shown in Fig. 3 are rearranged in terms of the rate enhancement given by the ratio of R_{deg} at the TiO_2/mordenite to that at unsupported TiO_2 as a function of the ratio of the amount of substrates adsorbed on mordenite to that on TiO_2 particles (S_{ads}(mor)/S_{ads}(TiO_2)). The results are shown in Fig. 6. The ratio of S_{ads}(mor)/S_{ads}(TiO_2) was obtained by using the data given in Table 1 and Eqs. 1 and 2. It is noticed from the figure that the rate enhancement rapidly grows with an increase of the ratio of S_{ads}(mor)/S_{ads}(TiO_2). It is recognized from the results on adsorption equilibrium of propionaldehyde shown in Fig. 1 that the ratio of S_{ads}(mor)/S_{ads}(TiO_2) increased with a decrease of the gaseous concentration of the substrate. The same was true for the other two kinds of substrates of acetone and propane. Therefore, the results given in Fig. 6 indicate that the rate enhancement of photodegradation is higher at lower concentrations of the substrates at the TiO_2/mordenite photocatalysts regardless of the kind of substrates used, though the dependence of the rate enhancement on the ratio of S_{ads}(mor)/S_{ads}(TiO_2) were different among the kinds of substrates. Presumably both the diffusibility of the substrates in the photocatalyst film and their reactivities on the TiO_2 surface affect such concentration dependence on the photodegradation rate, but details are not known at the present stage.

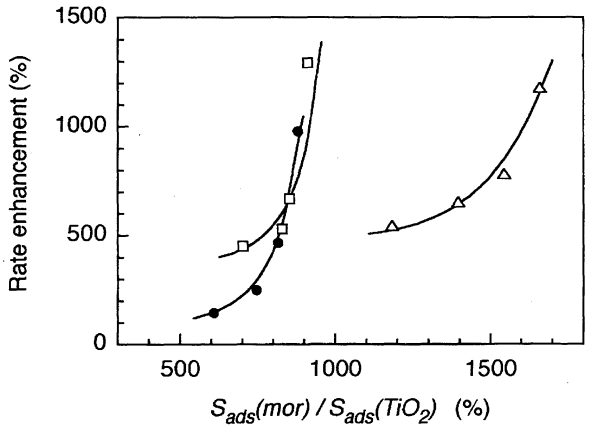

Fig. 6. Enhancement effect of the initial photodegradation rates as a function of S_{ads}(mor)/S_{ads}(TiO_2) for propionaldehyde (□), acetone (●), and propane (△).

Conclusion

In this study, the effects of a mordenite support for a TiO_2 on increasing the photodegradation rate of substrates were clarified as a function of the substrate concentration for three kinds of substrates. The apparent photodecomposition rates of gaseous substrates at the TiO_2-loaded mordenite photocatalyst increases with an increase of their adsorption on mordenite supports, but the enhancement of the photodecomposition rate caused by the mordenite support is more significant for lower concentrations of substrates used. Accordingly TiO_2-loaded adsorbent photocatalysts will be useful in the practical application such as the purification of contaminated air which contains extremely low concentrations of organic pollutants in a ppm level or below.

We acknowledge the financial support from the Ministry of Education, Science, Sports and Culture. N. T. is grateful to Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

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